DETERMINATION OF THE THERMAL DIFFUSIVITY OF EDIBLE FILMS

S.A. Tomás[1,4], A. Cruz-Orea[1], S. Stolik[2], R. Pedroza-Islas[3], D.L. Villagómez-Zavala[3] y C. Gómez[3]

[1] Departamento de Física, CINVESTAV-IPN, AP 14-740, México 07360 D.F., México

[2] Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear, 5ta y 30, No. 502, Miramar, Playa, La Habana, Cuba

[3] Universidad Iberoamericana, Departamento de Ingeniería y Ciencias Químicas. Prol. Reforma 880, Lomas de Santa Fe, México 01210 D.F., México

[4] To whom correspondence should be addressed. Email: stomas@fis.cinvestav.mx

ABSTRACT

One of the most important factors in the preparation of edible films regards the choice of ingredients. Edible films are commonly prepared with single or mixed high-molecular-weight compounds like proteins and gums. In the present work, protein and gum-based edible films were prepared and their thermal diffusivity determined by photoacustics. The films were prepared with different concentrations of four basic ingredients: mesquite gum, whey protein concentrate, sodium alginate and κ-carrageenan. In single-component films, the highest thermal diffusivity was found in mesquite gum (1.97 x10^{-7} m^2/s), followed by sodium alginate, whey protein concentrate and κ-carrageenan samples. In composed films, the highest thermal diffusivity was obtained in the mesquite gum-whey protein concentrate-alginate mixture (5.20 x10^{-7} m^2/s).

1. INTRODUCTION

The development and characterization of edible films have increasingly attracted the attention of biochemists, biotechnologists, and physicists, among others, mainly due to the large variety of applications served by these polymers. Particularly, the capability of edible films to regulate moisture, lipid migration, and gas transport, can be used to improve food quality and extend the shelf life of foodstuff. In addition, edible films play an important role in the covering of thermolabile compounds like vitamins, aroma, and flavors, providing an efficient method to preserve their characteristics during food processing.

One of the most important factors in the preparation of edible films regards the choice of ingredients. In the last few years, the use of biomolecules, e.g. proteins, lipids, and polysaccharides, has received special attention. Protein-based films have been prepared with both vegetal and animal proteins [1], including corn zein, soy protein [2,3], wheat proteins (gluten, gliadin) [4-6], peanut protein [7], gelatin, casein [8,9], and milk whey proteins [10,11]. On the other hand, edible coatings and films based on polysaccharides have been mainly used for fruit covering due to their excellent selective permeability to O_2 and CO_2. These low-cost films are mostly prepared with derivatives of cellulose, starch, pectins, and gums [12].

A number of studies have also been devoted to the characterization of the mechanical properties [13,14], and the lipid and flavor permeability of edible films [15]. On the contrary, less attention has been paid to the thermal characterization, in spite of its importance, specially when these films are used for covering thermolabile compounds. In the present work, we determine the thermal diffusivity of composed and single-component polysaccharide-based films

(mesquite gum, sodium alginate, and κ-carrageenan) and analyze the effect of adding whey protein concentrate to them.

2. MATERIALS AND METHODS

2.1. Chemicals

κ-carrageenan (C) was obtained from Germantown (Mexico), sodium alginate (Na-A) from Colloids Naturels de Mexico (Mexico), and whey protein concentrate at 80% protein (WPC) from Ingredientes Funcionales de Mexico (Mexico). Mesquite gum (MG) was collected in San Luis Potosí, Mexico and purified as described by Vernon-Carter et al. [16]. Sorbitol was used as plasticizer (sorbitol: solids content; 0.35:0.65 ; w:w).

2.2. Sample preparation

Single-component aqueous dispersions (component : distilled water; 0.025 : 0.975; w:w) were prepared with a homogenizer (Polytron, Model PT MR 2100) at 25,000 rpm for 90 s. Mixtures of these dispersions were then prepared according to the simplex lattice design [17] (see Table 1). For WPC samples, dispersions were heated in a water bath at 90 °C for 30min [18]. The Na-A and C dispersions were heated in water at 60 °C. The MG dispersions were heated at 80 °C for 30 min to denaturalize their protein fraction [19]. The plasticizer was added to degassed dispersions, and the product was degassed once again. Finally, 20 mL of the dispersions were spread onto rimmed, smooth teflon casting plates of about 14 cm internal diameter, which were placed on a leveled surface at room temperature (20 ° C and 35± 5% RH).

2.3. Photoacoustic measurements

The thermal diffusivity of edible films was determined by photoacoustics, specifically, we used the open photoacoustic cell (OPC) method. This method consists in mounting the sample onto the front sound inlet of a cylindrical electret microphone in such a way that a photoacoustic (PA) cell is formed by the sample and the interior walls and membrane of the microphone [20,21]. A chopped light beam of appropriate wavelength is used to excite the sample. When non-radiative de-excitation processes take place, different mechanisms of heat generation can be observed, e.g., thermal diffusion, thermoelastic bending and thermal expansion. Depending on the chopper frequency of the light beam, thickness and thermomechanical properties of the samples, one or more of these mechanisms can contribute to the PA signal [21-23].

2.3.1. Experiment

The experimental set-up employed to obtain the thermal diffusivity (α) of the samples consisted of a 100 mW Ar laser whose light beam was mechanically modulated with a chopper. The sample was fixed with vacuum grease upon the inlet of an electrect microphone. The microphone output signal was amplified with a lock-in amplifier and the PA amplitude and phase were measured as a function of the chopper frequency. The PA signal was generated either by thermal diffusion or the thermoelastic bending effect. We describe below both kinds of mechanisms.

2.3.2. Thermal diffusion mechanism

In the thermally thick region, i.e., when the sample thickness (l) is larger than the thermal diffusion length $(\alpha/\pi f)^{1/2}$, the thermal diffusivity can be obtained by fitting the PA amplitude (S) to the expression [21,24,25]:

$$S = (A/f) \exp (-a \; f^{1/2}) \qquad\qquad (1)$$

Here, A depends on the light beam intensity, room temperature, geometric constants, and thermal parameters. The coefficient a is related to the thermal diffusivity according to $a=l(\pi/\alpha)^{1/2}$.

2.3.3 Thermoelastic bending mechanism

In the OPC configuration, the thermoelastic bending mechanism predicts a *1/f* frequency dependence of the PA amplitude [23]. The ratio of the thermoelastic to the thermal diffusion contributions depends on α and the thermal expansion coefficient (α_t), as well as on geometrical factors. The thermoelastic bending effect dominates at high frequencies because the thermal diffusion contribution is exponentially damped out. In the thermally thick regime, the expression for the phase of the thermoelastic signal is [22]

$$\varphi = \pi/2 + \arctan \{ \; 1 \; / \; (z{-}1) \; \} \qquad\qquad (2)$$

where $z=l(\pi f /\alpha)^{1/2}$, indicating that α can be obtained from the frequency dependence of the PA phase.

3. RESULTS

The thermal diffusivity of the analyzed films is presented in Table 2. The highest value, 5.20 x10^{-7} m^2/s, corresponded to the film with mesquite gum, whey protein concentrate, and sodium alginate, in identical parts (treatment 6). As an evidence of the strong dependence of the films on the constituents and treatment, we refer to sample 15. Although a ternary sample, constituted by whey protein concentrate, sodium alginate and κ-carrageenan in identical amounts, this polymer

had a thermal diffusivity of 0.15 x 10^{-7} m^2/s. For single-component films, the highest thermal diffusivity was obtained in MG films (1.97 x 10^{-7} m^2/s) followed by the Na-A, WPC, and C films, with values 1.34x10^{-7}, 0.71x10^{-7}, and 0.40x10^{-7} m^2/s, respectively. These differences can be attributed to the type of molecules that constitute the film, as well as to their chemical bounding, which gives place to different types of chain packaging that modify the availability of unoccupied volume in the polymer matrix [26].

Plots of the thermal diffusivity as a function of the constituent concentration, for ternary films, are shown in Fig. 1. The higher thermal diffusivity values occurred in ternary mixtures where the carrageenan or alginate were absent, whereas in mixtures where MG (Figure 1 a) or WPC (Figure 1 c) were not present the thermal diffusivity was lower. The films with lower thermal diffusivity consisted of binary mixtures of carrageenan and sodium alginate. In this binary film, the thermal diffusivity decreased as the carrageenan content dominated the mixture (see Fig. 1a and 1c). High values of α are observed when MG and C ingredients are present in the film, at low proportions of Na-A (Figure 1 c). In the case of Na-A and C mixtures, the addition of WPC led to an increment of α values (Figure 1 a).

4. DISCUSSION

The study of interactions between milk whey proteins and polysaccharides has received special attention. The combination of these compounds form a complex protein-polysaccharide system, whose interactions are different from the individual properties of their components [27]. In the case of sodium alginate-protein films, Veliky [28] has reported that a gel structure of this system

is different to the alginate gel alone. This author mentions that the concentration of polysaccharide also has an effect on the system, because a denser membrane is formed when the polysaccharide is increased. Such membrane assists the polysaccharide-polysaccharide interactions rather than the protein-polysaccharide interactions. The interactions between polysaccharides are expected to improve the thermal conductivity and the thermal diffusivity of the sample. It is also important to consider electrostatic interactions between both types of molecules [29]. In agreement with Chaparro-Mercado [30], a dispersion of Na-A and WPC has a pH around 5.78, which corresponds to a value slightly higher than the isoelectric point (Ip) of the milk whey proteins. This gives the film a negative charge, similarly to Na-A, favoring electrostatic repulsion and, as a consequence, the formation of aggregates. Under these circumstances, the proteins tend to aggregate and distribute inside the gel. This could explain the decrease of the thermal diffusivity when the Na-A content increases in the WPC binary mixture (Table 2).

The carrageenan is also an anionic polysaccharide with sulfate groups and produce aqueous dispersions with pH values around 7 [30]. When C is mixed with proteins, specifically with WPC, with a pH higher than the Ip of the protein, they could form soluble complexes [31]. When the WPC content prevails over C in this mixture and the pH fulfills the mentioned condition, carrageenan drops are spread in a continuous whey protein gelled network [32]. This continuous network assists higher thermal conductivity and thermal diffusivity values. On the contrary, when C is present in a higher proportion than WPC, there is not diffusion of C in the milk whey proteins. It increases the aggregation of WPC, producing sites with micro separation of phases in the network [33]. These inhomogeneities in the network certainly tends to decrease the thermal conductivity and thermal diffusivity.

The MG and WPC interaction occurs at pH values below the Ip of milk whey proteins, because the MG dispersions have a pH value around 4. In these conditions, the proteins are positively charged and the MG has a slightly negative charge [16], which favors the formation of a protein-polysaccharide complex that tends to improve the thermal conductivity and the α values as the proportion of WPC is increased in the mixture. For an excess of WPC, α decreases gradually to reach the WPC α value.

Polysaccharides mixtures produces an increase in the thermal diffusivity (Figure 1c). In this case, the higher concentration of some components in the mixture also assists the aggregation between molecules of the same component. The mechanism of association could be through hydrogen bonds [34]. Finally, when identical amounts of WPC, Na-A, C and MG were included in the film (treatment 25) the thermal diffusivity was clearly diminished.

REFERENCES

1. A. Gennadios, T.H. McHugh, C. Weller, and J.M. Krochta, in *Edible Coatings and Films to Improve Food Quality*, J.M. Krochta, E. Baldwin, and M. Nisperos-Carriedo, eds. (CRC Press, USA, 1994), pp. 201-278.

2. J.W. Rhim, A. Gennadios, A. Handa, C. Weller, and A. Milford, *J. Agric. Food Chem.* **48:** 4937 (2000).

3. S.K. Park, C.O. Rhee, D.H. Bae, and N.S. Hettiarachchy, *J. Agric. Food Chem.* **49**: 2308 (2001).

4. L.M. Rayas, R.J. Hernandez, and K.W. Perry, *J. Food Sci.* **62**:160 (1997).

5. N. Gontard, S. Guilbert, and J.L. Cuq, *J. Food Sci.* **58**: 206 (1993).

6. T.J. McMaster, M.J. Miles, L. Wannerberger, A.N. Eliasson, P.R. Shewry, and A.S. Tatham, *J. Agric. Food Chem.* **47**: 5093 (1999).

7. A. Jangchud and M.S. Chinnan, *J. Food Sci.* **64**: 153 (1999).

8. J.J. Avena-Bustillos and J.M. Krochta, *J. Food Sci.***58**: 904 (1993).

9. J.J. Avena-Bustillos, J.M. Krochta, and M.E. Saltviet, *J. Food Sci.* **62**:351 (1997).

10. M. Anker, M. Stading, and A.M. Hermansson, *J. Agric. Food Che.* **48**: 3806   (2000).

11. R. Sothornvit and J.M. Krochta, *J. Agric. Food Chem.* **48**: 3913 (2000).

12. M. Nisperos-Carriedo, in *Edible Coatings and Films to Improve Food Quality*, J.M. Krochta, E. Baldwin, and M. Nisperos-Carriedo, eds. (CRC Press, USA, 1994), pp. 305-335.

13. S. R. Park, C.O. Rhee, D.H. Bae, N. S. Hettiarachhy, *J. Agric. Food Chem.*, **49:** 2308-2312 (2001).

14. J.W. Rhim, A. Gennadios, A. Handa, C.L. Weller, M.A. Hanna, *J. Agric. Food Chem.,* **48,** 4937-4941 (2000).

15. K.S. Miller and J.M. Krochta, *Trends Food Sci. Technol.* **8**: 228 (1997).

16. E.J. Vernon-Carter, C.I. Beristain, and R. Pedroza-Islas, in *Novel Macromolecules in Food Systems,* G. Doxastakis and V. Kiosseoglou, eds. (Elsevier, Amsterdam, 2000), pp. 217-238.

17. D.C. Montgomery, in *Diseño y análisis de experimentos,* (Grupo Editorial Iberoamericano, México, 1991), pp. 494-500.

18. T.H. McHugh, J.F. Aujard, and J.M. Krochta, *J. Food Sci.* **59**: 416 (1994).

19. E.J. Vernon-Carter, S.A. Gómez, C.I. Beristain, G. Mosqueira, R. Pedroza-Islas, and R. Moreno-Terrazas, *J. Texture Studies* **27**: 625 (1996).

20. I. Delgadillo, A. Cruz-Orea, H. Vargas, A. Calderón, J. J. Alvarado-Gil, L.C.M. Miranda, *Opt. Eng.*, **36**, 343-347 (1997).

21. A. Garcia-Quiroz, S. A. Tomás, H. Vargas, A. Cruz-Orea, L. Veleva, J. J. Alvarado Gil, L. C. M. Miranda , *Instrumentation Science and Technology*, **26**: 241-260 (1998).

22. N. F. Leite, N. Cella, H. Vargas, L.C.M. Miranda, *J. Appl. Phys.*, **61**: 3025-3027 (1987).

23.- A. M. Mansanares, A.C. Bento, H. Vargas, N. F. Leite, L.C.M. Miranda, *Phys. Rev. B*, **42**: 4477(1990)

24.-M E. Rodríguez, J.M. Yáñez, A. Cruz Orea, J.J. Alvarado Gil, O. Zelaya Angel, H. Vargas, Sánchez Sinencio, J.D. Figueroa, F. Martínez-Bustos, J.L. Martínez-Montes, J. Gonzalez-Hernandez, L.C.M. Miranda, Z. *Lebens. Unter. Forsh*, **201**: 236-240 (1995).

25.- L. Veleva, , S. A Tomas Velásquez, A. Cruz-Orea, I. Delgadillo, H. Vargas, E. Marín, J. J. Alvarado-Gil,. P. Quintana, R. Pomes, L. C. M. Miranda, *Corrosion Science*, **39**: 1641-1655 (1997).

26.- D.H. Weinkauf and D.R. Paul, in: *Barrier polymers and structur,* W. Koros, ed. (American Chemical Society, Washington, 1990), pp. 60-91.

27.- S.K. Samant, R.S. Singhal, P.R.Kulkarni, and D.V. Rege, *Int. J. Food Sci. Tech*. **28**, 547-562 (1993).

28.- I.A. Veliky, Monograph Am. Oil Chem., **11:** 37 (1984).

29. A. Martinsen, I. Storro, and G. Skjak-Braek, *Biotechnol. Bioeng.* **39**, 186-194 (1992).

30.-M.C. Chaparro-Mercado, Determinación del tipo de ligante óptimo en dietas microparticuladas para larvas de camarón. M. Sc. Thesis. Universidad Iberoamericana. México. (2003).

31.-V.B. Tolstoguzov, in: *Functional properties of food macromolecules*. S. E. Hill, D. A. Ledward and J. R. Mitchell, eds. (Aspen Publishers, Inc. Maryland, 1998), pp. 253-277.

32.- E. Dumay, A. Laligant, D. Zasypkin, and J.C. Cheftel, *Food Hydrocol.* **13,** 339-351 (1999).

33.- I. Capron, T. Nicolai, and D. Durand, *Food Hydrocol* **13**: 1-5 (1999).

17. 34.- P. Williams, and G.O. Phillips, in: *Food polysaccharides and their applications*. A. Stephen, ed., (Marcel Dekker, Inc. USA. 1995), pp. 463-497
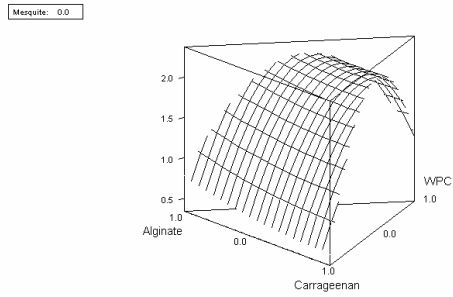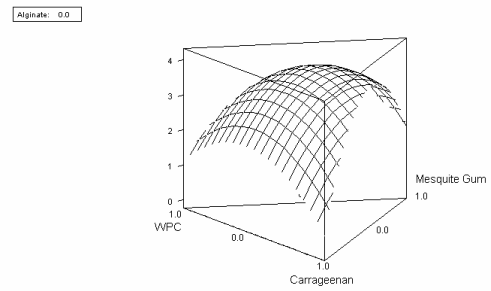
(a) without Mesquite Gum
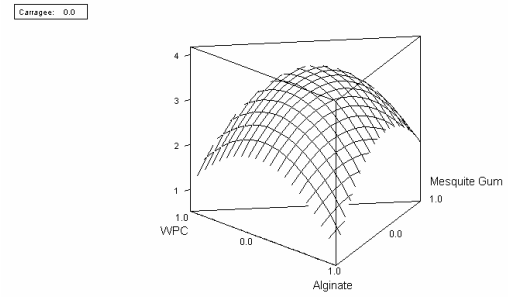
(b) without Carrageenan
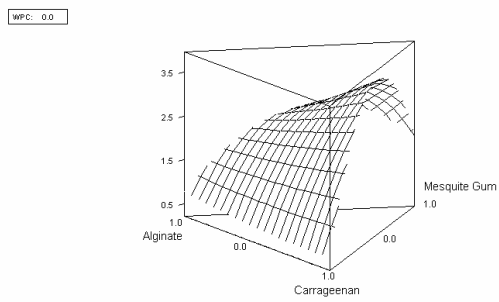
(c) without WPC

(d) without Alginate

Figure 1. Surface response of thermal diffusivity for the case of ternary mixtures.

Table 1. Edible films prepared with mesquite gum, whey protein concentrate, sodium alginate and κ-carrageenan.

Treatment	Mesquite gum	WPC	Na-Alginate	κ-Carrageenan
1	1.0000	0.0000	0.0000	0.0000
2	0.6650	0.3350	0.0000	0.0000
3	0.6650	0.0000	0.3350	0.0000
4	0.6650	0.0000	0.0000	0.3350
5	0.3350	0.6650	0.0000	0.0000
6	0.3330	0.3330	0.3330	0.0000
7	0.3330	0.3330	0.0000	0.3330
8	0.3350	0.0000	0.6650	0.0000
9	0.3330	0.0000	0.3330	0.3330
10	0.3350	0.0000	0.0000	0.6650
11	0.0000	1.0000	0.0000	0.0000
12	0.0000	0.6650	0.3350	0.0000
13	0.0000	0.6650	0.0000	0.3350
14	0.0000	0.3350	0.6650	0.0000
15	0.0000	0.3330	0.3330	0.3330
16	0.0000	0.3350	0.0000	0.6650
17	0.0000	0.0000	1.0000	0.0000
18	0.0000	0.0000	0.6650	0.3350
19	0.0000	0.0000	0.3350	0.6650
20	0.0000	0.0000	0.0000	1.0000
21	0.2500	0.2500	0.2500	0.2500
22	0.6250	0.1250	0.1250	0.1250
23	0.1250	0.6250	0.1250	0.1250
24	0.1250	0.1250	0.6250	0.1250
25	0.1250	0.1250	0.1250	0.6250

Table 2. Thermal diffusivity of the edible films of Table 1.

Treatment	Thermal diffusivity x 10^{-7} ($m^2 s^{-1}$)	Treatment	Thermal diffusivity x 10^{-7} ($m^2 s^{-1}$)
1	1.97	14	1.10
2	2.76	15	0.15
3	3.39	16	2.36
4	3.60	17	1.34
5	3.30	18	1.04
6	5.20	19	0.75
7	3.80	20	0.40
8	0.33	21	0.27
9	3.07	22	1.99
10	3.32	23	1.68
11	0.71	24	1.92
12	2.85	25	0.72
13	2.85		